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Light-chromatic identification of rare-earth luminescent fibres doped with organic onium salt

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Organic onium salt has been used as a photosensitive pigment for rare-earth luminescent fibre. A certain dose of organic onium salt has been added to rare-earth strontium aluminate luminescent fibre (RESALF) during its melt spinning. Its photochromatic property is studied by comparing RESALFs with and without the organic onium salt. RESALF photochromatic identification method is devised according to the Standard Colorimetric System CIE (International Commission on illumination) 1931 XYZ. The results show that, when excited by 365nm wavelength light, RESALF doped with organic onium salt exhibits good photochromatic properties. The luminescence color of RESALF doped with organic onium salt switches from the yellow-green region to the blue region. The light-chromatic recognition method used is thus able to provide an accurate identification of the luminescence color of the new RESALF.

Keywords: Organic onium salt, Photochromatic property, Rare-earth luminescent fibre

1 Introduction

As the most commonly used light-storing luminescent fibre, RESALF (rare-earth strontium aluminate luminescent fibre) is distinguished by its excellent afterglow property, good ultraviolet resistance, and reliable chemical stability¹⁻⁴. However, expanding and enriching the luminous color of RESALF remains a difficult and key issue. As a typical inorganic photo-luminescent substance, rare-earth strontium aluminate luminescent is a luminescence source, which can be excited by 365nm wavelength exciting light to emit the 520nm wavelength (yellow-green) light. If mixed with inorganic transparent pigments of different colors, it may possibly produce colorful luminescent RESALF products^{5, 6}. Former studies indicated that inorganic pigments added during the melt spinning of RESALF can change its excitation spectrum, to a certain extent, and modify its photochromatic distribution. However, the inorganic pigments do not emit light by themselves. Instead, they absorb part of its glow to reduce its brightness to a certain extent. This means that the currently available pigments do not possess good photochromatic properties. Therefore, a new

type of photochromic material needs to be sought to produce a photochromic effect on rare-earth fibres without affecting the brightness of the fibre.

Photochromatic substances can be divided into two categories, viz organic and inorganic materials. Based on the differences in their structures, they could be further classified into different types. Onium salt photochromatic substances are non-toxic and odorless with excellent heat stability, wear resistance, good photo-transformation and chemical stability. They are able to produce active free radicals and chromosphere through photodecomposition, to transform light from one wavelength to another⁷. Moreover, as compared to conventional organic pigments, onium salt photochromatic substances, which can be excited by lights of various wavelengths and hardly be subjected to photo-degradation, possess wider absorption spectrums and higher fluorescence quantum yields. Therefore, they have a more stable luminescent property, and will play a significant role in the color-changing technology of luminescent materials.

The pigment for RESALF doped with the onium salt is a kind of organic-inorganic hybrid whose luminescence is caused by both rare-earth strontium aluminate and the onium salt. Therefore, the identification of the hybrid's photochromism and the realization of datamized simulation have become the

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major issues in this study. After abandoning the old-fashioned visual observation method for color identification, subsequent datamized color processing methods, including the RGB color space method, the fuzzy C means clustering algorithm method, the HIS color space method, the k means Hierarchical Clustering method and the LVQ (learning vector quantization) neural network method have emerged⁸⁻¹³. However, these methods were not able to fully and objectively distinguish colors, and certain limitations still remain. In 1853, H. Grassmann proposed the Grassmann color law, which states that almost all colors can be obtained by mixing the three primary colors at different ratios¹⁴. This law also applies to photochromism. Color distinguishing of RESALF allows the determination of the glow color of the fibre in a spectrum under conditions with no light, and it can be realized using the Grassmann color law.

This study is aimed at introducing a new type of photochromatic fibre produced by adding an onium salt, and triarylsulfonium hexafluoroantimonate salt (THS), into a rare-earth strontium aluminate luminescent material via melt spinning. The micro-morphological features and photochromatic property of the new fibre can be better analyzed under a scanning electron microscope (SEM), a spectrum analysis apparatus and other necessary tools. The effects of the doped organic onium salt on the new fibres' photochromatic property has been studied by comparing the new fibre with normal polypropylene fibres and original RESALF with the organic onium salt, to establish a rational and effective method for distinguishing the glow color of photochromatic fibres.

2 Materials and Methods

2.1 Materials

Potassium iodate, benzene, acetic anhydride, potassium hexafluoroantimonate, diphenyl sulfide

and cupric acetate anhydrous, all of AR grade, were purchased from Dingmiao Chemical Limited, Shanghai. Concentrated sulfuric acid and anhydrous acetonitrile, both of AR grade, were obtained from Sinopharm Chemical Reagent Co Ltd. PP slice (great light M P 165°C) was obtained from Wuxi Taichu Group. Rare earth luminescent material (colorless, $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$) was obtained from Changshu Jianghui Fiber Products Technology Co, Ltd.

2.2 Preparation of Organic Onium Salt

Potassium iodate, benzene, acetic anhydride and solvent (anhydrous acetonitrile) were placed in a round bottom flask, added concentrated sulfuric acid very slowly using a dropper, and left the mixture to react for 2 h under an ice-salt bath conditions. Then, the mixture was stirred and allowed to react further at room temperature (20-25°C) for 48 h. When the temperature decreased to -5 °C again, a certain amount of potassium hexafluoro antimonate aqueous solution was added. Thus, the white crystalline diaryliodonium hexafluoro-antimonate was prepared through the process of suction filtration, washing and recrystallization.

The above product (diaryliodonium hexafluoro-antimonate white crystal), phenyl sulfide and an appropriate amount of catalyst were sequentially added to a round bottom flask. Heated the liquid to 100~120 °C using nitrogen gas and allowed it to react for 3 h. Finally, dried in an oven to obtain triaryl hexafluoroantimonate white crystal through the process of suction filtration, washing and recrystallization again. Figure 1 shows the specific chemical reactions.

2.3 Preparation of RESALF Doped with Organic Onium Salt

RESALF doped with organic onium salt is prepared using the melt spinning method. PP slice, THS, and rare-earth strontium aluminate luminescent were placed together at a predetermined ratio into a

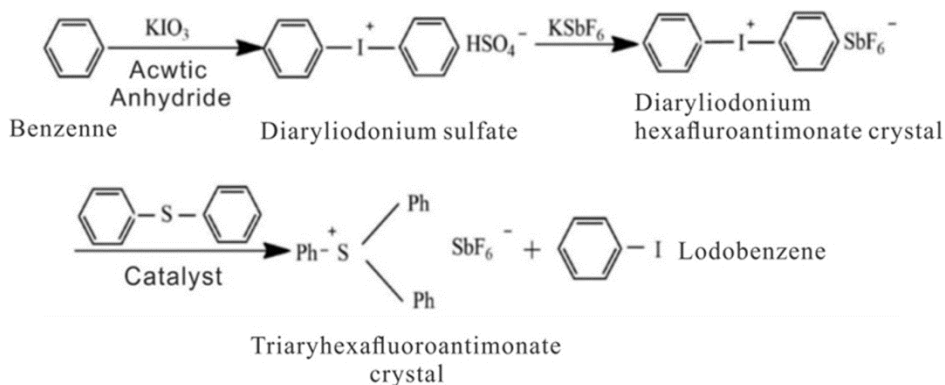


Fig. 1 — Chemical reaction of triaryl sulfonium hexafluoroantimonate.

melt spinner, and melted at temperatures between 220°C and 250°C. The molten material was extruded into rare-earth fibre samples using a double screw extruder by pulling and winding. Table 1 shows the parameters used for the preparation of RESALF doped with organic onium salt.

2.4 Test Method

The surface morphology of THS was observed using a scanning electron microscope (Model: Quanta 200) provided by FEI company (Netherlands). THS was dried and put through a metal spraying process before being tested at a voltage of 20kV.

The chromaticity coordinates of RESALF doped with organic onium salt were determined by a PR-650 radiation spectrum analyzer provided by Zhejiang University SENSING (Hangzhou) Instrument Co., Ltd. Light source of the test was D65, a CIE standard light source, and the test visual angle was 10°.

3 Results and Discussion

3.1 Micro-morphology Analysis

Figure 2 (a) shows the SEM diagram of the grounded and sieved THS. It shows that THS consists of irregularly shaped white grains with sharp edges, and the size of the grain is within the range of 1-8µm. These characteristics meet the requirements for pigments of RESALF.

Figure 2 (b) shows RESALF doped with organic onium salt with the diameter of 20 µm. The fibre has a rough surface, uniform thickness and good filamentation. The surface of the fibre includes irregularly distributed granular substances, which are supposed to be rare-earth strontium aluminate granules rather than the organic onium salt according to Fig. 2 (a). This is due to the melting temperature of 220-250 °C, which is significantly higher than THSs peak melting temperature of 166°C, as shown in Fig. 3 (a). Furthermore, Fig. 3 (b) shows that THS has excellent thermal stability, with the main weight loss occurring at 413 °C, and decomposition beginning after heating at 275 °C. This is consistent with the spinning temperature of the polypropylene substrate. This further demonstrates that THS can be added

as a dopant to the spinning raw material of the polypropylene substrate.

3.2 Photochromatic Property

In order to facilitate the identification and calculation of the luminescent color of the rare earth luminescent fibre added with THS, a light-color discrimination method based on the CIE 1931 XYZ standard chromaticity system¹⁴⁻¹⁶ has been designed from the perspective of standard colorimetry. The discrimination method is a partition query method can calculate the slope using color coordinates. Moreover, the proposed light color recognition method provides a theoretical basis for the development of blue luminous fibre and the standardization of technology, which can quickly and effectively determine the luminous color of the luminous fibre.

Figure 4 indicates the samples chromaticity coordinates and their vector diagrams of color light. RESALF doped with organic onium salt, original RESALF (without organic onium salt) , onium salt and rare-earth strontium aluminate luminescent material have been used for photochromatic test one by one using a spectrum analyzer, to obtain 4 sets of chromaticity coordinates, according to which the four samples could be located in the CIE1931 chromaticity diagram. For each sample, within the CIE color space, the straight line connecting its location-point and the light-source point E extend to and intersect with the spectrum locus, and their intersection is the primary wavelength of the sample. According to the color light mixing law, a drawing is thus produced using the

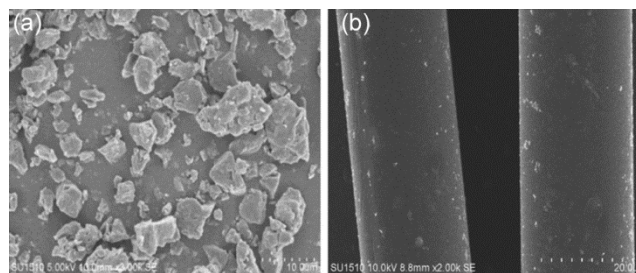


Fig. 2 — SEM image (a) triaryl sulfonium hexafluoroantimonate and (b) luminescent fibre by doping with triaryl sulfonium hexafluoroantimonate

Table 1 — Manufacturing method of luminescent fibre doped with triaryl sulfonium hexafluoroantimonate

| Method | Raw material formula | Spinning temperature, °C | Stretch multiple |
|--------|--|--------------------------|------------------|
| 1 | PP:Rare-earth luminescent material: Organic strontium salt =95%:5%:0% | 250 | 2.9 |
| 2 | PP:Rare-earth luminescent material: Organic strontium salt=94.5%:5%:0.5% | 250 | 2.9 |

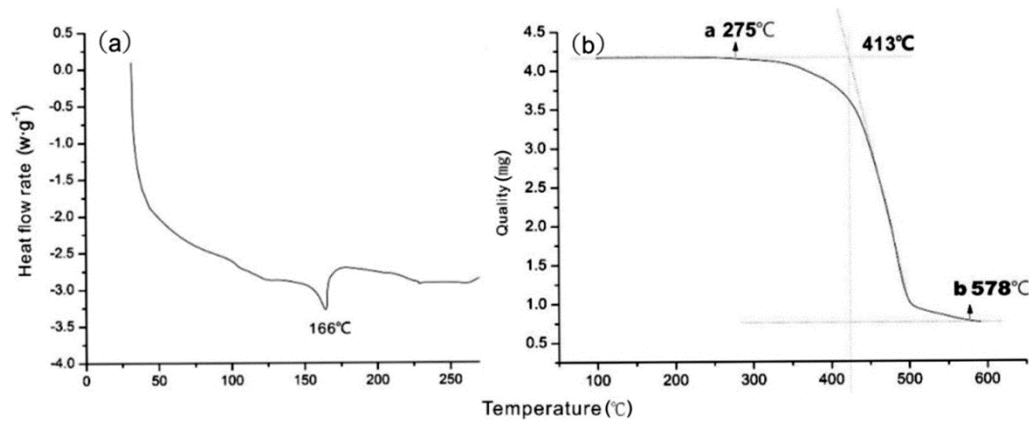


Fig. 3 — Thermal performance analysis curve of triaryl sulfonium hexafluoroantimonate (a) differential scanning calorimeter diagram and (b) heat loss curve diagram.

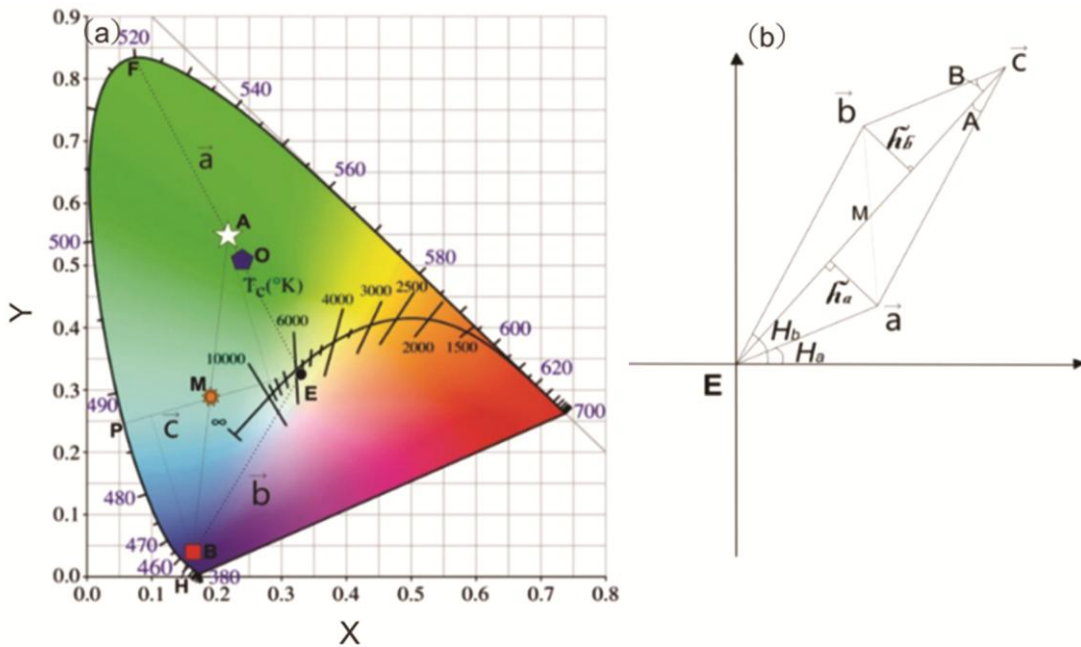


Fig. 4 — Chromaticity coordinates (a), and light color vector map (b) of the sample

vector addition method to plot the area of light color of RESALF doped with organic onium salt.

The chromaticity coordinate of the sample is illustrated in Fig. 4 (a) in which A is the chromaticity coordinate of the rare-earth luminescent material, and B is the chromaticity coordinate of THS. As the light color of RESALF doped with organic onium salt is produced from additive mixing of the light color of THS and that of the rare earth luminescent material, as shown in Figure 4 (b), the location of RESALF doped with organic onium salt (M) can be plotted on the CIE1931 diagram using the light color addition method. The process to determine M by plotting is given hereunder:

- Connect the rare earth luminescent material's chromaticity coordinate (vector \vec{a}), and THS's chromaticity coordinate (vector \vec{b}) in Fig. 4 (b) to form a straight line.
- In the vertical straight line of the middle vector (\vec{c}), between \vec{a} and \vec{b} , plot a pair of vectors (\vec{h}_a and \vec{h}_b), that are equal in size but opposite in directions .
- For $h_a = h_b$ (the modules of \vec{h}_a and \vec{h}_b), draw a straight line connecting the intersection points of the vertical line in \vec{h}_a and \vec{h}_b .
- Extend the straight line until it intersects with the other straight line connecting \vec{a} and \vec{b} at Point M ,

which is located in the blue-light region. The point is the chromaticity coordinate of RESALF doped with organic onium salt.

According to the vector diagram of the samples area, the other module of \vec{c} can be deduced from a vector synthesized from \vec{a} and \vec{b} by addition, as shown below:

$$c = \sqrt{a^2 + b^2 + 2ab\cos\theta} \quad \dots (1)$$

Phase formula of \vec{c}

$$B = \arccos\left(\frac{a+b\cos\theta}{b\sin\theta}\right) \quad \dots (2)$$

$$B = \arctan\left(\frac{b\sin\theta}{a+b\cos\theta}\right)$$

Therefore, the color phase of the synthesized vector is:

$$H_c = H_b + B \quad \dots (3)$$

where c is the synthesized vector of a and b ; H_b , the THS's color phase; B , the chromaticity coordinate of THS.

Furthermore, in Fig. 4 (a) which shows the chromaticity coordinate map of the sample, another straight line is drawn to connect the light source E and Point M. The straight line is extended further until it intersects with the spectrum diagram at Point P. This point is the primary wavelength of RESALF doped with organic onium salt, which is within the blue-light region near 487nm. Similarly, another straight line is drawn to connect the light source Point E and Point O. The straight line is extended until it intersects with the spectrum diagram at Point F (520 nm); F represents the primary wavelength of original RESALF without organic onium salt. The wavelength variation indicates that the light color of RESALF doped with organic onium salt approaches the blue light region further than that of original RESALF. This is due to the conjugate double bond existing in the new RESALF that is able to absorb UV light and emit 440nm wavelength blue-light [refer to sample B in Fig. 4 (a)]. This indicates that THS adds a tinge of blue to the original color of RESALF. At the same time, according to the chromaticity coordinate values on the CIE1931 chromaticity diagram, the samples' saturation can be obtained by calculation, and the saturation formula of RESALF doped with organic onium salt is as follows:

$$P_m = \frac{\overline{EM}}{\overline{EP}} = \frac{x_m - x_e}{x_p - x_e} \quad \dots (4)$$

where P_m is the saturation formula of RESALF; \overline{EM} , the horizontal chromaticity coordinate values from point M to E; \overline{EP} , the horizontal chromaticity coordinate values from point P to E; and x_e , x_p and x_m , the horizontal chromaticity coordinate values of Point E, P and M respectively. According to the photo-chromaticity tristimulus formula, the following calculation can be realized:

$$\begin{cases} x = \frac{X}{X+Y+Z} \\ y = \frac{Y}{X+Y+Z} \\ z = \frac{Z}{X+Y+Z} \end{cases} \quad x+y+z=1$$

$$\begin{cases} x = \frac{X}{X+Y+Z} = \frac{0.490r + 0.310g + 0.200b}{0.667r + 1.132g + 1.200b} \\ y = \frac{Y}{X+Y+Z} = \frac{0.177r + 0.812g + 0.010b}{0.667r + 1.132g + 1.200b} \\ z = \frac{Z}{X+Y+Z} = 1 - x - y \end{cases} \quad \dots (5)$$

The chromaticity coordinate of the light source is determined, where Point E is $x_e, y_e = (0.327, 0.325)$, and the chromaticity coordinate of Point P is $x_p, y_p = (0.0573, 0.2492)$. Moreover, the photochromatic saturation of RESAF doped with organic onium salt, original RESALF, THS and rare earth luminescent materials can be calculated using Eq.(4). Figure 4 (a) clarifies the samples chromaticity coordinates: Point F, $x_f, y_f = (0.0695, 0.8334)$, and Point H, $x_h, y_h = (0.1595, 0.0334)$. Having determined the chromaticity coordinates of Sample A, B, O and M, using the spectrum analyzer, the samples photochromatic chromaticity coordinates and saturation are determined, as shown in Table 2.

Table 2 shows that the spectrum analysis result of Point M is close to the chromaticity coordinate determined using the vector color addition method. This means that the chromaticity value of a luminescent fibre doped with an organic substance can be determined through the method. The photochromatic saturation of the samples depends on the fullness of their color. The table shows that the saturation of rare-earth luminescent material is higher than that of original RESALF, and the saturation of THS is also higher than that of doped RESALF. In general, the photochromatic saturation (purity) is decided by coloring the element and decolorizing the element ratio in the photochromatic color. The

Table 2 — The color coordinates and saturation of sample

| Sample | CIE chromaticity coordinates | | Saturation P % |
|---|------------------------------|--------|-------------------|
| | x | y | |
| Rare-earth luminescent material (Sample A) | 0.2354 | 0.5532 | 34.80 |
| Triaryl sulfonium hexafluoroantimonate (Sample B) | 0.1798 | 0.0476 | 87.73 |
| Rare-earth fiber without organic cerium salt (Sample O) | 0.2469 | 0.5045 | 30.33 |
| Rare-earth fiber doped with organic cerium salt (Sample M) | 0.1902 | 0.2943 | 49.98 |

higher purity indicates higher saturation and more colorizing elements. Therefore, it can be explained that the light colors of SrAl_2O_4 : Eu^{2+} , Dy^{3+} luminescent materials and triarylsulfonium hexafluoro-antimonate are highly saturated with respect to the luminous fibres. Different saturation results in different color phases, meaning that organic onium salts can enrich the color catalogue of photochromatic fibres.

3.3 Photochromatic Stimulation of RESALF Doped with Organic Onium Salt

This part will introduce a method to determine the location of RESALF doped with organic onium salt in the CIE color space by slope calculation through color area division based on the spectrum chromaticity coordinate. The specific process of the method is as follows:

Calculate the spectrum locus (x , y) and the slope of the white point (x_e , y_e), using the following formula:

$$k = \frac{y - y_e}{x - x_e} \quad \dots (6)$$

where k refers to the slope of the sample. The chromaticity coordinate of Point E can be calculated using the tristimulus specified by CIE1931, it is $x_e = 0.327$, $y_e = 0.325$. Subsequently, divide the chromaticity diagram into 9 areas according to the slope-wavelength relationship. Table 3 shows slope of chromaticity graph and color classification criteria.

As shown in Table 3 and according to the X axial and corresponding slope ranges, the CIE1931 chromaticity diagram can be divided into 9 areas. Each area, divided according to a slope determined by a tristimulus calculation, corresponds to a color in the chromaticity diagram. The position of RESALF doped with organic onium salt can then be determined

Table 3 — Slope of chromaticity graph and color classification criteria

| Partition | Color | X coordinate | Slope standard |
|-----------|--------------|--------------|----------------------------|
| 1 | Purple | $x > 0.327$ | $k \leq -0.1599$ |
| 2 | Red | $x > 0.327$ | $-0.1599 < k \leq 0.2591$ |
| 3 | Orange | $x > 0.327$ | $0.2591 < k \leq 0.8581$ |
| 4 | Yellow | $x > 0.327$ | $k > 0.8581$ |
| 5 | Yellow | $x < 0.327$ | $k \leq -4.2261$ |
| 6 | Yellow-green | $x < 0.327$ | $-4.2261 < k \leq -0.6476$ |
| 7 | Green | $x < 0.327$ | $-0.6476 < k \leq 0.1230$ |
| 8 | Blue | $x < 0.327$ | $0.1230 < k \leq 2.0738$ |
| 9 | Purple | $x < 0.327$ | $k > 2.0738$ |

according to the color-slope division. Figure 5 shows the division of the chromaticity diagram.

Figure 5 indicates that the 1931CIE chromaticity diagram has been divided into 9 areas. All spectrum colors are distributed inside or on the edge of the lingua shaped curve, and the wavelengths (400-700 nm) clockwise, are located in the purple, blue, green, yellow-green, yellow, orange, red regions successively, before returning back to the purple region again. The straight-line section, which is not shown in the spectrum, represents the region from purple to red, which corresponds to the color of crimson.

For this slope method, the modified RESALF (M) doped with organic onium salt, and original RESALF (O) are adopted. Before commencing slope calculation, the R, G, B values of M and O respectively shall be determined using the spectrum analyzer: for Point M -- R, G, B values are (0, 175, 213), for Point O -- R, G, B values are (159, 215, 0).

According to the standard illuminants recommended by CIE1931, chromaticity coordinates (r , g , b) of RESALF doped with organic onium salt, and original RESALF can be calculated using Eq (5). For Point O, r_o , g_o , $b_o = (0.4251, 0.5749, 0)$, and for Point M, r_m , g_m , $b_m = (0, 0.4083, 0.5917)$. Subsequently, convert the above chromaticity coordinates from the RGB

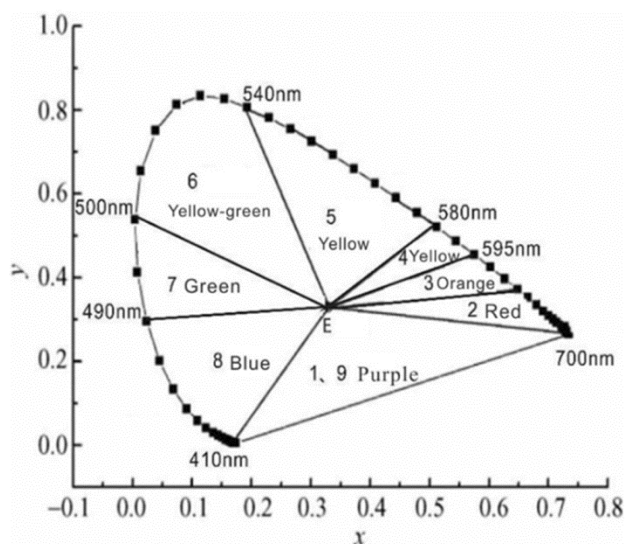


Fig. 5 — 1931CIE color segmentation

space to the XYZ space, and calculate the chromaticity coordinates (x , y) of Point O and Point M. For Point O, $x_o=0.2334$, $y_o=0.5002$, and for Point M, $x_m=0.1857$, $y_m=0.2846$.

Substituting the 1931CIE-XYZ chromaticity coordinates determined above into Eq (6), the slopes, k_o and k_m , of the straight lines connecting Point O and Point M respectively can be calculated, and the light source point E: $k_o = -2.7265(-4.2261 < k \leq -0.6476)$, $k_m = 1.0882(0.1230 < k \leq 2.0738)$ can be determined. Referring to the standard for color-slope division of the chromaticity diagram (Table 3), it is observed that RESALF doped with organic onium salt sits within the 8th photochromatic region, which is a blue-light region, while original RESALF is in the 6th photochromatic region, which is a yellow-green light region. This result, in general, agrees with that of the above-mentioned test-plotting method.

In general, the slope calculation and spectrum division methods are rather accurate in the identification of chromaticity coordinates.

4 Conclusion

4.1 The organic onium salt in the preparation has a grain size no larger than $10\mu\text{m}$, which fulfils the related requirement for melt spinning. The photo-luminescent RESALF is good at producing fibre, and the finished product contains grains of the rare-earth strontium aluminate luminescent material distributed within it or on its surface.

4.2 During the preparation of the photochromatic

fibre, RESALF's photo-chromic property has been effectively improved through a synergistic interaction between the organic onium salt and the rare-earth strontium aluminate luminescent material. The chromaticity value for RESALF doped with organic onium salt falls in the blue-purple region on the chromaticity diagram, highlighting its displacement from the yellow-green region where the rare-earth strontium aluminate luminescent material.

4.3 Through the test-plotting method, we find that the chromaticity value for RESALF doped with organic onium salt falls in the blue-light region; the same result is derived through the slope-division method. Therefore, the test result and the simulation result have demonstrated that the chromaticity value for RESALF doped with organic onium salt has moved towards the blue light region. Moreover, the slope simulation method which prevents fuzzification of luminescent fibre chromaticity identification can be used as a module for the identification of the rare-earth fibre photo-chromaticity theory, and has a potential value for further application.

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